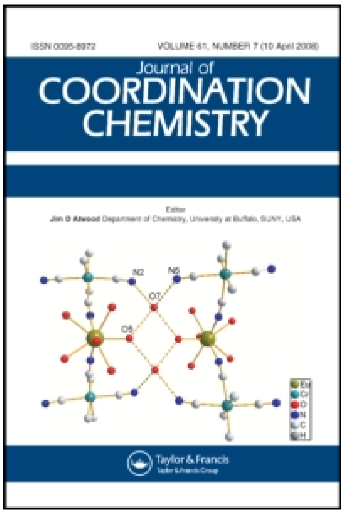

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

AG(I)-N-METHYLSUBSTITUTED 1,3-DIAMINOPROPANE COMPLEXES IN 1 M NO_3^-

R. Garner[a]; J. Yperman[a]; J. Mullens[a]; L. C. Van Poucke[a]
[a] Laboratory of Inorganic and Physical Chemistry, Limburgs Universitair Centrum, Diepenbeek, Belgium

To cite this Article Garner, R. , Yperman, J. , Mullens, J. and Van Poucke, L. C.(1994) 'AG(I)-N-METHYLSUBSTITUTED 1,3-DIAMINOPROPANE COMPLEXES IN 1 M NO_3^-', Journal of Coordination Chemistry, 31: 2, 117 — 123
To link to this Article: DOI: 10.1080/00958979408024207
URL: http://dx.doi.org/10.1080/00958979408024207

J. Coord. Chem., 1994, Vol 31, pp. 117–123
Reprints available directly from the publisher
Photocopying permitted by license only

AG(I)-N-METHYLSUBSTITUTED 1,3-DIAMINOPROPANE COMPLEXES IN 1 M NO_3^-

R. GARNER, J. YPERMAN, J. MULLENS and L.C. VAN POUCKE*

Laboratory of Inorganic and Physical Chemistry, Limburgs Universitair Centrum,
B-3590 Diepenbeek, Belgium

(Received April 2, 1993)

The complexation behaviour of a number of *N*-methylpropylene diamines with Ag(I) were studied in 1 M KNO_3 at 25.00°C potentiometrically, employing pH and pAg measurements. Several metal/ligand ratios were used (varying from 2/1 to 1/8). Complexation of these ligands with Ag(I) in aqueous solution is described by the following species: AgL, AgLH, AgL_2, AgL_2H, AgL_2H_2, Ag_2L_2 and Ag_2L_2H. No mixed ligand hydroxo species could be detected in the concentration employed. Stability constants of a given species systematically decrease as methylation increases on the terminal amino groups due to increased steric effects.

KEYWORDS: *N*-methylpropylenediamines, aliphatic diamines, silver stability constants

INTRODUCTION

Some forty years ago Schwarzenbach[1] proposed a dimeric species Ag_2L_2 between ethylenediamine and Ag(I) but he did not find such a species for 1,3-propylenediamine.[2] Since then, a number of papers have been published on the subject, with that of Ohtaki et al.[5] being the most recent for aqueous solutions. The models, species and constants found in the literature on the complexation of Ag(I) with 1,3-propylenediamine (or trimethylenediamine -TN-) are surveyed in Table 1. To our knowledge there have been no attempts to determine the formation constants of this metal ion with any of the *N*-methyl derivatives.

In this work the following complexes of 1,3-diaminopropane derivatives with Ag(I) were investigated in 1 M KNO_3: 1,3-diaminopropane (TN), *N*-methylpropylenediamine (MTN), *N,N'*-dimethylpropylenediamine (SDIMTN), *N,N*-dimethylpropylenediamine (ADIMTN), *N,N',N'*-trimethylpropylenediamine (TRIMTN) and *N,N,N',N'*-tetramethylpropylenediamine (TETMTN).

Symbols

C_{Ag}, C_L and C_H are the total concentration of silver, ligand and proton and [Ag], [L] and [H] are the free concentrations of silver, ligand and proton.

---

* Author for correspondence.

Table 1 Literature values for the formation constants of 1,3-propanediamine complexes with Ag(I); log units.

	reference 6–7	reference 5	reference 4	reference 3	reference 2
solvent	DMSO:25°C	H_2O:25°C	H_2O:25°C	H_2O:25°C	H_2O:20°C
ionic strength	0.1 M NEt_4ClO_4	3 M $LiClO_4$	1 M KNO_3	-> 0.0	0.1 M $NaNO_3$
data type	pAg data	pH data	pH and pAg data	pH data	pH and $[Ag^+]$ = constant
C_{Ag}/C_L ratio	variable	1/2–1/16	±1/25	1/2–1/2.5	10/1–20/1
species:					
AgL	5.9(2)	6.59	6.7	5.92	5.8
AgL_2		9.8	7.85		(7.7)
AgLH		14.32	13.99		13.2
AgL_2H_2		28.90	24.79		
AgL_2H		19.2(5)			
AgL(OH)		-3.5(7)			
Ag_2L	8.06(9)				6.4
Ag_2L_2	14.4(2)	15.90			

The general reaction between a metal ion, a proton and ligand is usually expressed as

$$pM + qL + rH \leftrightharpoons M_pL_qH_r \qquad \beta_{pqr} = \frac{[M_pL_qH_r]}{[M]^p[L]^q[H]^r}$$

where β_{pqr} is the formation constant of the complex $M_pL_qH_r$. (for $r < 0$ hydroxo complexes and $r > 0$ protonated complexes are formed)

The relative complexation function is $\eta = \log(C_M/[Ag])$. A plot of this function *vs* number of base equivalents is more informative than pAg/base equivalents as one can directly estimate how much silver is complexed.

EXPERIMENTAL

Reagents

$AgNO_3$ (Merck p.a.) and KNO_3 (Merck p.a.) were used without further purification. KOH and HNO_3 solutions were prepared from Titrisol ampoules (Merck p.a.). KOH solutions were prepared under an N_2 atmosphere with freshly boiled, doubly distilled, deionized water and kept under a CO_2-free atmosphere in a polyethylene bottle (used within two weeks of preparation). The ionic strength of all solutions was kept constant with KNO_3 at 1M NO_3^-.

The following diamines were purchased in the amine form: 1,3-diaminopropane (Aldrich Chem., 99%), *N*-methyl-1,3-diaminopropane (Aldrich Chem., 99%), *N,N'*-dimethyl-1,3-diaminopropane (Aldrich Chem., 97%), *N,N*-dimethyl-1,3-diaminopropane (Janssens Chem., 99%), *N,N,N'*-trimethyl-1,3-diaminopropane (Aldrich Chem., 98%) and *N,N,N',N'*- tetramethyl-1,3-diaminopropane (Janssens Chem., 99%) and were neutralized with 2 equivalents HNO_3. The corresponding dinitrate salts were purified by repeated crystallization from EtOH and dry dimethylether and dried on P_4O_{10} in a vacuum desiccator.

Calibration

The following electrodes were used: a glass electrode (Ingold pH 0-14 U262-S7), a reference electrode (Ingold Argental 363-S7) in a saltbridge (Schott-Geräte B511 with ceramic plug) filled with 1.5 M KNO_3 and an Ag/Ag_2S electrode (Orion 94-16). EMF values of the glass electrode were recorded with a Radiometer PHM 64/84 instrument with a resolution of 0.1 mV. Corresponding pAg measurements were performed with an Orion 94-16 Ag/Ag_2S electrode with a resolution of 0.01 mV.

The calibration of the glass and the Ag/Ag_2S electrode, experimental set-up, temperature control, equilibrium criteria used for the electrodes, determination of the electrode characteristics, determination of the pK_w (13.775 ± 0.003) and pK_A values of the *N*-methylsubstituted-1,3-propylenediamines were as described in previous papers[8-10].

Complexation titrations

Several different C_{Ag}/C_L ratio's were employed, 2/1, 1/1, 1/2, 1/4 and 1/8, in order to obtain the largest diversity of complexes. Two main stock solutions were used, 0.01 M $LH_2(NO_3)_2$ in 0.98 M KNO_3 (ligand solution) and 0.01 M $AgNO_3$ in 0.99 M KNO_3 (silver solution).

Ratio's 1/1 - 1/2 - 1/4 - 1/8 were obtained by keeping the number of mmol of ligand constant and varying the volume of the silver solution added to the mixture. The initial volume of the mixture was kept constant by adding 1 M KNO_3. The 2/1 ratio was prepared by using 20 cm^3 of the ligand solution and 40 cm^3 of the silver solution. All solutions were added to the titration vessel using precise burettes instead of pipettes. The obtained solution was titrated (0.1 M KOH in 0.99 M KNO_3) until both protons were liberated from the ligand or until precipitation occurred. This can be noted by either erratic electrode response or visually. Precipitation generally occurred with the high C_{Ag}/C_L ratio: 2/1 and occurred sooner as the number of methyl groups on the amine function increased.

Titration points with an ionic product $[Ag^+][OH^-] > 10^{-7.3}$ were excluded from the calculations to make sure that the pK_s of Ag_2O[11] was not exceeded. It is of prime importance to make sure that all mass balances remain accurate for all titration points in a one-phase system. All titrations are performed at least in duplicate. Calibration of the glass electrode and the Ag/Ag_2S electrode was performed externally before and after each titration.

Calculations

The obtained data were analysed using Superquad.[12-14] Several models were tested using the weighted option in Superquad ($\sigma_{E\ glass} = 0.2$ mV, $\sigma_{E\ Ag/Ag_2S} = 0.1$ mV and $\sigma_V = 0.002$ mL). Possible complex species considered were AgL, AgLH, AgL_2, AgL_2H, AgL_2H_2, Ag_2L, Ag_2L_2, Ag_2L_2H, Ag_2L_3, AgLOH and AgL_2OH. Model-selection- criteria were a good overall fit (fit-statistic S[13] should be less than 3), a low standard deviation of the constant, a significant % species presence (an arbitrary minimum value of 3%) and a minimum number of species.

Acidity constants, pK_w, mass balances and electrode parameters were kept constant during model refinement. All calculations were performed at double precision. Diagrams were made using the Disspla drawing package. Listings of all programs, including those used for graphical analysis, are available from the authors.

RESULTS AND DISCUSSION

A list of the formation constants of the best models is presented in Table 2. As an example, the data of ADIMTN have been fitted with the obtained constants and are shown in Figures 1 and 2. We define the following equilibria and their constants to make further discussion more clear.[15-16].

$$\begin{array}{lll}
AgL + L \leftrightharpoons AgL_2 & K_2 = \beta_{120}/\beta_{110} & (1) \\
Ag + LH \leftrightharpoons AgLH & K_{111} = \beta_{111}/\beta_{011} & (2) \\
AgL + H \leftrightharpoons AgLH & K'_{111} = \beta_{111}/\beta_{110} & (3) \\
Ag + LH + L \leftrightharpoons Agl_2H & K_{121} = \beta_{121}/\beta_{011} & (4) \\
AgL_2 + H \leftrightharpoons AgL_2H & K'_{121} = \beta_{121}/\beta_{120} & (5) \\
AgLH + LH \leftrightharpoons AgL_2H_2 & K_{122} = \beta_{122}/(\beta_{111} \cdot \beta_{011}) & (6) \\
Ag + 2LH \leftrightharpoons AgL_2H_2 & K'_{122} = \beta_{122}/\beta^2_{011} & (7) \\
AgL_2 + Ag \leftrightharpoons Ag_2L_2 & K_{22} = \beta_{220}/\beta_{120} & (8) \\
Ag_2L_2 + 2L \leftrightharpoons 2\ AgL_2 & K'_{22} = \beta^2_{120}/\beta_{220} & (9) \\
2\ AgL \leftrightharpoons Ag_2L_2 & K_d = \beta_{220}/\beta^2_{110} & (10)
\end{array}$$

Charges are omitted for clarity. Stability constants corresponding to the above reactions are presented in Table 3 and are given in log units.

Mononuclear protonated complexes: $AgLH$ and AgL_2H_2

AgLH is the only species that is encountered in each model. Comparing K_{111} for each ligand, we note a systematic decrease in value as the number of methyl groups increases on the terminal amino groups. AgLH is the first species to be formed when the first proton is liberated from the ligand. As such, it gives a picture of the average

Table 2 A survey of the formation constants (in log units), standard deviations (in brackets) and maximum % species present of *N*-methyl-substituted propylenediamines with Ag(I) using the weighted option in Superquad.

	TN	%	MTN	%	ADIMTN	%	SDIMTN	%	TRIMTN	%	TETMTN	%
Species:												
AgL					3.55	14			2.91(1)	24	2.21(*)	21
AgL_2	7.81(1)	16	7.37(1)	23	7.11(*)	78	6.27(*)	10	5.52(2)	15		
AgLH	13.75(*)	20	13.62(*)	20	12.81(*)	23	13.13(*)	16	12.20(*)	10	11.26(*)	5
AgL_2H_2	27.72(*)	20	27.69(*)	35	25.86(*)	20	26.37(*)	6				
AgL_2H			17.68(2)	9	16.70(1)	21						
Ag_2L_2	14.86(*)	98	13.50(*)	92	11.02(*)	51	12.12(*)	96	9.61(*)	41		
Ag_2L_2H			21.19(3)	4								
S-statistic	2.07		3.04		1.58		1.00		1.80		1.45	
# titration points	764		731		666		628		396		398	
# data points	1528		1462		1332		1256		792		796	

* Less than 0.01.

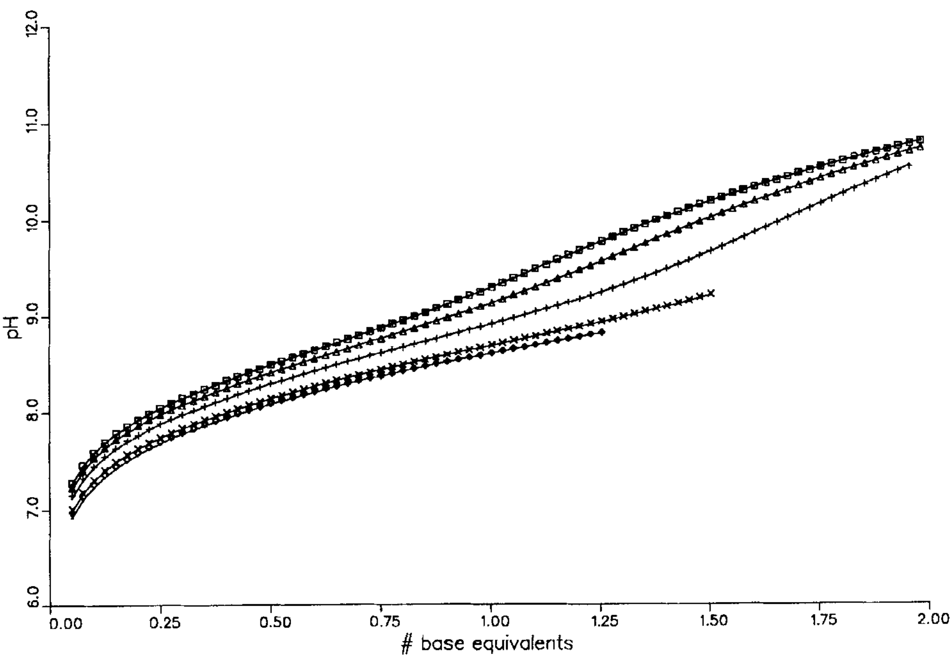

Figure 1 The pH data from the complexation of ADIMTN with Ag(I) *vs* number of base equivalents using ratios 1/8 (□), 1/4 (△), 1/2 (+), 1/1 (x), 2/1 (◇). The full line is the fitted curve using the formation constants from Table 2.

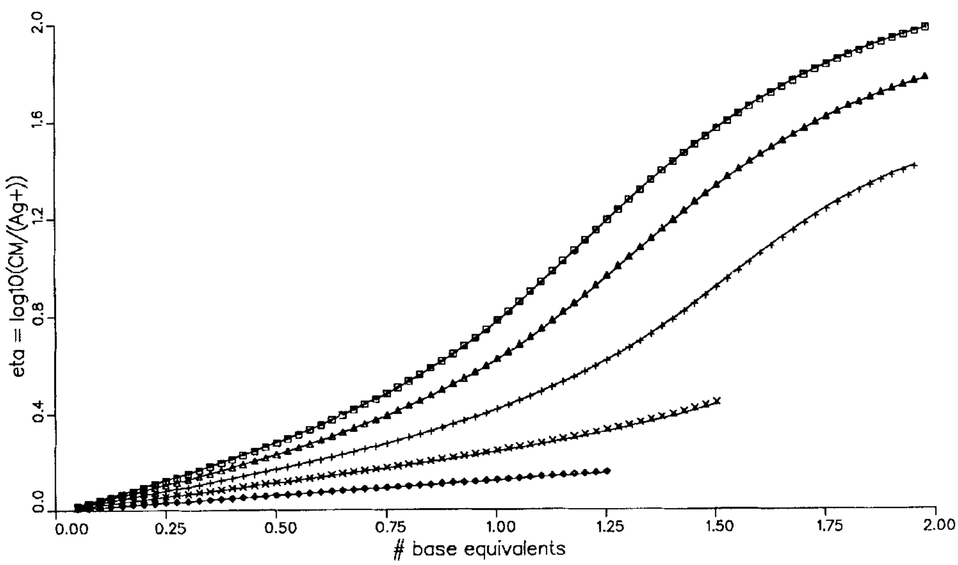

Figure 2 Relative complexation function from the complexation of ADIMTN with Ag(I) *vs* number of base equivalents using ratios 1/8 (□), 1/4 (△), 1/2 (+), 1/1 (x), 2/1 (◇). The full line is the fitted curve using the formation constants from Table 2.

Table 3 Stability constants corresponding to the reactions (*1*) to (*10*).

	TN	MTN	ADIMTN	SDIMTN	TRIMTN	TETMTN
K_2			3.56		2.61	
K_{111}	3.01	2.75	2.35	2.21	1.56	1.21
K'_{111}			9.26		9.29	9.05
K_{121}		6.80	6.24			
K'_{121}		10.31	9.58			
K_{122}	3.23	3.19	2.58	2.32		
K'_{122}	6.24	5.94	4.93			
K_{22}	7.06	6.13	3.91	5.86	4.10	
K'_{22}	0.74	1.24	3.21	0.41	1.43	
K_d			3.92		3.79	

availability of a first N-atom for complexation; LH seems to react like a monoamine. First, the values of K_{111} are of the same magnitude as the first complexation step of a secondary monoamine like diethylamine with Ag(I) ($\beta_{110} = 3.1$)[9,17] and decrease to a value typical of a tertiary monoamine like trimethylamine with Ag(I) ($\beta_{110} = 1.7$)[9,17]. We would normally expect for propylenediamine a value of the magnitude of a primary monoamine ($\beta_{110} = 3.4$)[9,17] because it does not have any hindering methyl groups. The proton left on the ligand is able to destabilize the species through $Ag^+ \leftarrow L{-}H^+$ repulsion, an effect suggested by Ohtaki et al.[5] Secondly, the stability constants for the equilibrium defined by K_{122} are systematically larger than the corresponding K_{111}. This is generally attributed to primary and secondary monoamine silver complexes but is also observed in the complexation of alcoholamines with Ag(I).[9,17]

Non-protonated complexes: AgL, AgL_2 and Ag_2L_2

The species AgL is not detected for TN, MTN and SDIMTN. The results of TN can be compared with those of one of the authors[20] for the complexation of ethylenediamine with Ag(I). The latter could not detect AgL species either. The large formation constants for the dimeric species Ag_2L_2 might be the reason for the undetectability of AgL.

As Cassol et al.[7] point out, the higher formation constant for Ag_2L_2 for TN (14.86) in comparison with EN[20] (13.15), can be explained by the 12 membered ring of the dimeric species of TN with Ag(I) that resembles more closely the linear N-Ag-N configuration than does a 10 membered ring with EN. Another explanation is that the Ag^+ -Ag^+ repulsion in the dimeric ring of TN is decreased in comparison with EN due to the larger distance between the two complexated Ag^+ ions in the dimeric ring of TN. Because we only have stability constants of AgL for 2 ligands, ADIMTN and TRIMTN, we can calculate the dimerization constant K_d solely for these two ligands.

The systematic decrease mentioned earlier in the formation constants of AgLH is also visible in the constants of AgL_2 except with TETMTN where the species is not formed. The formation constants of the dimeric species also decrease as the number of methyl groups increase, but the situation is reversed with SDIMTN and ADIMTN. This can be understood by looking at equilibrium (*9*) and the corresponding constant K'_{22}. The equation describes the tendency of the dimeric species to form the more stable species AgL_2. ADIMTN has the highest value in the Table.

This is presumably the result of the combination of a tertiary amine and a primary amine on the ligand. The tertiary amine will block dimerization through steric effects while the primary amine will try to form AgL_2. Blocking by the tertiary amine of dimerization is indicated by the fact the TETMTN gave no dimeric species. It is interesting to note that values for K'_{22} for the symmetric ligands TN and SDIMTN are of the same order whereas they are somewhat higher for the other ligands.

Other complexes: AgL_2H and Ag_2L_2H

These species never become predominant and should be regarded as intermediates between AgLH, AgL_2H_2 and Ag_2L_2 and AgL_2. There are too few values to form any conclusions concerning these constants.

Two main conclusions can be drawn from these results. The stability of a given species decreases as the number of methyl groups on the amine functions increases. In addition, the number of formed species also decreases as branching on the complexing N-atoms increases.

References

1. G. Schwarzenbach and H. Ackermann, *Helv. Chim. Acta*, **35**, 2337(1952).
2. G. Schwarzenbach and B. Maissen, *Helv. Chim. Acta*, **35**, 2333 (1952).
3. C.R. Bertsch and W.C. Fernelius, *J. Phys. Chem.*, **62**, 444 (1958).
4. P. Lanza, *J. Electroanal. Chem.*, **19**, 289 (1968).
5. H. Ohtaki and K. Cho, *Bull. Chem. Soc. Jpn.*, **50**, 2674 (1977).
6. A. Cassol and P. Di Bernardo, J. Chem. Soc. Dalton Trans., 1781 (1988).
7. A. Cassol and P. Di Bernardo, J. Chem. Soc. Farad. Trans. I, 2445 (1989).
8. R. Garner, J. Yperman, J. Mullens and L.C. Van Poucke, *Bull. Soc. Chim. Belg.*, **102**, 3 (1993).
9. R. Garner, J. Yperman, J. Mullens and L.C. Van Poucke, *J. Coord. Chem.*, in press.
10. R. Garner, J. Yperman, J. Mullens and L.C. Van Poucke, *F.J. Anal. Chem.*, **347**, 145 (1993).
11. C.F. Baes and R.E. Mesmer, *Hydrolysis of Cations*, (Wiley, New York, 1976), p. 124.
12. P. Gans and A. Sabatini, *Inorg. Chim. Acta*, **79**, 219 (1983).
13. P. Gans and A. Sabatini, *J. Chem. Soc. Dalton Trans.*, 1195 (1985).
14. P. Gans, *Data Fitting in the Chemical Sciences*, (Wiley, Chichester, 1992).
15. J. Yperman, J. Mullens, J.P. François and L.C. Van Poucke, *Inorg. Chem.*, **22**, 1361 (1983).
16. J. Yperman, J. Mullens, J.P. François and L.C. Van Poucke, *Talanta*, **31**, 735 (1984).
17. R.M. Smith and A.E. Martell, *Critical Stability Constants, Volume 2, Amines*, (1975) *Volume 5, First Supplement*, (1982), *Volume 6, Second Supplement*, (1989), (Plenum Press, New York).
18. L.C. Van Poucke and Z. Eeckhaut, *Bull. Soc. Chim. Belges*, **81**, 363 (1972).
19. I. Granberg and W. Forsling, *Acta Chem. Scand.*, **A36**, 819 (1982).
20. L.C. Van Poucke, *Talanta*, **23**, 161 (1976).